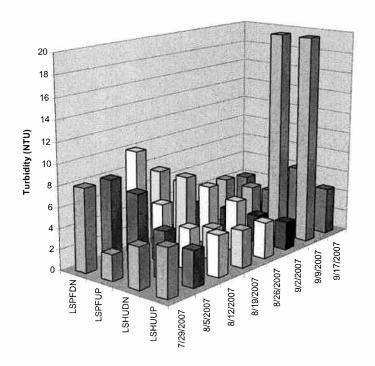
Quality Assurance Project and Sampling Plan

Water Quality Evaluation of the Lower Little Susitna River

July 2008

(Revision Number 2.0)







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A1. Water Quality Evaluation of the Lower Little Susitna River

| Aquatic Restoration and Re | | |
|----------------------------|--------------------------|-----------------------------|
| Project Manager: | for C Dani | Date: 7/31/08 |
| Quality Assurance Officer: | for C San gay a davis | Date: 4/31/08 |
| | | |
| Alaska Department of Envir | onmental Conservation | |
| Project Manager: Lun | _ Keller | Date: 8/12/08 |
| Quality Assurance Officer: | Janua Jandson | Date: <u>8/14/08</u> |
| Effective Date: | | |

A2. Table of Contents

| A2. | Table of Contents | 2 |
|-------|--|----|
| | Distribution List | |
| A4. | Project/Task Organization | 4 |
| | Problem Definition/Background | |
| A6. | Project/Task Description | 5 |
| A7. | Quality Objectives and Criteria for Measurement of Data | 9 |
| A8. | Special Training Requirements/Certification Listed | 11 |
| A9. | Documentation and Records | 12 |
| B1. | Sampling Process Design | 13 |
| B2. | Sampling Methods Requirements | 17 |
| B3. | Sample Handling and Custody Requirements | 19 |
| B4. | Analytical Methods Requirements | 19 |
| | Quality Control Requirements | |
| | Instrument/Equipment Testing, Inspection, and Maintenance Requirements | |
| | Instrument Calibration and Frequency | |
| B8. | Inspection/Acceptance Requirements for Supplies and Consumables | 22 |
| B9. | Data Acquisition Requirements for Non-Direct Measurements | 22 |
| B10. | Data Management | 22 |
| C1. | Assessments and Response Actions | 22 |
| C2. | Reports to Management | 23 |
| D1. | Data Review, Validation, and Verification | 23 |
| | Validation and Verification Methods | |
| D3. | Reconciliation with User Requirements | 24 |
| Liter | ature Cited | 25 |

A3. Distribution List

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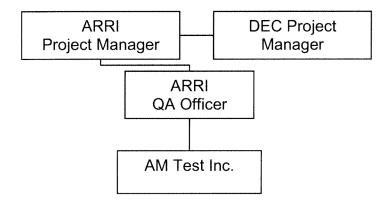
Mr. Jim Gendron **DEC Quality Assurance Officer** 410 Willoughby Ave., Ste 303 PO Box 111800 Juneau, AK 99811-1800 Ph: 907-465-5305

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A4. Project/Task Organization

The Project Manager listed below will be responsible for all project components including data collection, entry, analyses, and reports.

- Laura Eldred (DEC) DEC Project Manager. Ms. Eldred will oversee the project for DEC, provide technical support, QAPP review and approval, and the review of all quarterly reports and the final report.
- Jeffrey C. Davis (ARRI) Project Manager. Mr. Davis will make sure that all field data are collected as specified in the QAPP. He will test and maintain all equipment prior to use and perform the review of data entry and analyses.
- Gay A. Davis (ARRI) will act as Quality Assurance Officer. Ms. Davis will be responsible for making sure that all data are collected, replicate samples taken and analyzed, and all data entered and analyzed correctly.
- AM Test Inc.—Redmond, WA. The testing laboratory will be responsible for analyzing all collected water chemistry samples.



A5. Problem Definition/Background

The Little Susitna River flows from the Talkeetna Mountains to Cook Inlet. The river flows through the Hatcher Pass State Recreation Area, the residential communities of Wasilla and Houston, the Nancy Lake State Recreation Area and the Susitna Flats State Game Refuge. The Little Susitna River is one of the rivers managed under the Susitna Area Recreational Rivers Management Plan. The river supports a highly popular salmon and trout fishery as well as recreational non-motorized and motorized boating. There is a relatively high degree of residential development between Edgerton Park Road and Schrock Road, adjacent to the city of Wasilla, and the city of Houston. The lower river, from Houston to the Public Use Facility (PUF), is a popular recreational area for motorized and non-motorized boating, camping and sport fishing. Potential impacts to the lower river segment are from the residential development

adjacent to the city of Houston, and recreation, primarily boat-accessed sport fishing, with over 11,000 angler days in 2007 at the Public Use Facility. There are two areas of concentrated motor boat use, from Houston to Lake Creek and from 3 miles upstream of the public use site downstream to near Cook Inlet.

Recreation use also can cause an increase in sediment delivery rates and toxic hydrocarbons. Fine sediment delivery rates can increase with increasing bank failures due to the removal of bank vegetation with foot traffic. Boat waves also can increase bank failure rates and sediment delivery by eroding bank materials. Motor boats can deliver toxic hydrocarbons through fuel and oil leaks, spills or the inefficient combustion of engines, fuel spills, and bilge pumping.

Water quality sampling was conducted from July 2007 through June 2008 to determine the location and extent of potential hydrocarbon and turbidity contamination of the Little Susitna River. Sampling was conducted week through the fall coho fishery (July and August of 2007) and spring Chinook fishery (May and June of 2008) above and below the city of Houston and the Miller's Reach undeveloped boat launch and above and below the Public Use Facility. Preliminary results indicate total aromatic hydrocarbon concentrations exceeded state water quality standards adjacent to the Public Use Facility boat launch during the coho and Chinook fisheries. Stream water turbidities increased above background levels and periodically exceeded state standards.

The objectives of this project are to further identify the extent and duration of hydrocarbon contamination and changes in turbidity adjacent to the developed boat launch at the Public Use Facility. Hydrocarbon concentrations will be evaluated relative to boat use and motor type (2-cycle or 4-cycle engines), operation time, and stream flows. Secondary objectives include evaluating potential impacts to the macroinvertebrate and fish communities within affected areas.

A6. Project/Task Description Total Aromatic Hydrocarbons

This project has been designed to evaluate potential hydrocarbon contamination of the Little Susitna River and increases in turbidity near the public use facility. This will be accomplished by collecting water samples and analyzing them for Total Aromatic Hydrocarbons (TAH) and comparing to the State Water Quality Standard in 18 AAC 70. Water samples will be collected during times of heavy boat use during the recreational sport fisheries and during times of low boat use. Samples will be collected above and below high boat concentration use areas. Observations of boat motor type and duration within the sampling reach, and measures of discharge will be used to evaluate hydrocarbon inputs from boat use. Turbidity within heavy use areas will be compared to upstream reference locations.

OBJECTIVE 1: Quantify the spatial and temporal distribution of TAH concentrations adjacent to the public use facility and determine the relationship between 2-stroke motor use, stream flow, and TAH concentrations.

TASK 1: QAPP and Sampling Plan Approval

Start and end date: July 1, 2008 – July 31, 2008

Description: The ARRI project manager will modify the existing approved Quality Assurance Project Plan and Sampling Plan for DEC review and approval. Previously approved QAPP and Sampling Plan will be modified for the specific project tasks. These documents will describe in detail the frequency, duration, and location of all proposed sampling, including those listed under separate objectives. They will identify the equipment that will be used and how the equipment will be calibrated and maintained. It will describe the analytical methods that will be used and who will be handling and analyzing the water samples. The methods that will be used to determine data accuracy, precision, and completeness will be outlined. Data handling, management and reporting will be described. It will detail the responsibilities of all staff members and contractors and who will be responsible for each phase of the project. A draft QAPP and Sampling Plan will be completed within 3 days of receiving DEC authorization to work. The project manager will coordinate with the DEC project manager to address any inadequacies in the documents. ARRI will focus on completing this task as soon as possible.

Product: DEC approved QAPP and Sampling Plan.

TASK 2: TAH Sampling and Analyses

Start and end date: <u>July 1, 2008 – June 30, 2009</u>

Description: Water samples for TAH analyses will be collected at locations above and below the PUF during peak use times, and at a non-peak use time for comparison, that coincide with the fall coho salmon, and spring Chinook salmon fisheries. Fall sampling will begin in late July and extend through August. Spring sampling will begin in mid May and extend through June. Samples will be collected weekly on weekends, for seven weeks with more frequent sampling to coincide with peak use. Sampling locations will be at 1.0 km upstream of the PUF, 0.5 km upstream, at the PUF, 0.5 km downstream, 1.0 km downstream, 2.0 km downstream, and 4.0 km downstream. Water samples will be collected in sample containers provided by a commercial laboratory. Sampling will use the sampler and methods developed by the U.S.G.S. Samples will be preserved and shipped immediately to the laboratory for analyses. One duplicate sample will be collected and submitted on each sampling date. A portion of the sample also is held by the laboratory for repeat analyses if necessary. The laboratory will use EPA method 624 or as directed by DEC. The exact methodology will be described in detail within the QAPP and approved by DEC prior to beginning sample collection.

Product: Concentration of TAH and BETX during heavy use times at multiple locations surrounding the PUF. Data will be presented within the draft and final reports or as requested by the DEC project manager.

TASK 3: Determining 2-cycle (not fuel injected) Motor Use and Discharge

Start and end date: <u>July 1, 2008 – June 30, 2009</u>

Description: The most likely source of hydrocarbon input to the Little Susitna River will be quantified along with stream flow dilution. These parameters will be used to model expected concentrations to compare with analytical values. Model parameters include the size and running time 2-cycle engines are operating within the sampling reach. On water sampling dates, we will observe the boats at the launch, either leaving or returning, and report for each boat with a 2-cycle motor, motor size, and time (minutes) engine is running at launch. We will estimate the time within the reach based upon average time to travel 4 km. We also will obtain data from the entry station on the number of boats entering the launch on each sampling date, and if possible, the size and type of motor. Comparisons between our counts and the station counts will provide a check on the accuracy of observations. Discharge will be measured at 1.0 km upstream from the public use facility. We will obtain direct measures of discharge by wading when flows allow or by wading and boat when necessary.

Product: The relative number and use of 2-cycle motors in comparison to total number of boats and measures of discharge. A model of hydrocarbon inputs and a comparison with analytical measures. Data will be presented in the draft and final reports or as directed by the DEC project manager.

OBJECTIVE 2: Quantify changes in turbidity and determine if there are differences in the abundance of prey items or the catch rate of juvenile salmonids during the coho fishery above and below areas of peak use.

TASK 4: Quantify Changes in Turbidity

Start and end date: <u>July 1, 2008 – June 30, 2009</u>

Description: Turbidity within the Little Susitna River will be measured above and below the PUF during heavy use times. Turbidity would be measured from grab samples collected at times and location concurrent with TAH sampling. Turbidity also will be determined from continuous data loggers (HACH Mini-Sondes) placed upstream of the area of heavy use and at 1.0 km downstream from the PUF. Loggers will be deployed during and following concentrated use during the coho and Chinook fishery.

Product: Stream water turbidity comparing reference and potentially impacted stream reaches.

TASK 5: Evaluate the Abundance of Prey and Juvenile Salmonids

Start and end date: July 1, 2008 – June 30, 2009

Description: Sampling will be conducted to evaluate the relative catch rate of juvenile salmon and prey items in drift. Sampling will be conducted during peak boat use during the coho (fall 2008) and Chinook (spring 2009) sport fisheries at sampling locations above and within peak use areas. Juvenile salmon will be captured in baited minnow traps. Traps will

be placed on outside bends within areas of similar depth, velocity, and cover. Traps will be removed after 12 to 24-hours soak time. All captured fish will be counted, identified, and measured. Fish will be observed for DELT (Deformities, Eroded fins, Lesions, or Tumors) anomalies per U.S.G.S. methodology.

Macroinvertebrate drift is a measure of the relative food available for juvenile fish. Stream macroinvertebrates will be collected from drift nets placed above and within peak use areas. Drift nets will be placed just below the water surface. Nets will be left in place until debris within the mesh begins to diminish flows. Water velocity will be measured at the net opening at placement and prior to removal in order to calculate the total volume of filtered water. Samples will be combined for a composite for each site. All invertebrates within the sample will be identified to the lowest possible taxonomic level.

Product: The resulting data will be provided within the final report. Results will determine differences in biotic parameters between sites that have heavy boat use and adjacent reference sites.

OBJECTIVE 3: Obtain baseline measures of water chemistry and temperature.

TASK 6: Measure Basic Water Chemistry and Temperature

Start and end date: <u>July 1, 2008 – June 30, 2009</u>

Description: Water samples will be analyzed for pH, specific conductivity, and dissolved oxygen. Stream water temperature will be measured continuously using HOBO Water Temp pro data loggers. Water samples will be collected concurrently with samples collected for TAH and turbidity. Dissolved oxygen concentration, percent saturation, pH, and temperature will be measured in the field; specific conductivity and turbidity will be analyzed in the laboratory. Temperature data loggers will be placed upstream and at 1 km downstream from the PUF. Loggers will be placed in an area that is well mixed and will record temperature at 15 minute intervals. More details on sampling methods, sample locations, sample frequency and sample analyses will be provided within the QAPP and adjusted as directed by the DEC project manager.

Product: Basic water chemistry and temperature data at a reference location and at a recreational use area. Data will be presented in draft and final reports.

TASK 7: Data Formatting for STORET, Draft and Final Reports

Start and end date: June 1, 2009 – June 30, 2009

Description: Sampling locations, dates, methods, and resulting measurement values will be formatted for uploading into the STORET database. Data will either be transferred to DEC or uploaded by ARRI staff.

Draft and final written reports will be prepared. The final report will provide background information and describe the project need, objectives, and the approach that was taken to meet the objectives. Field methods will be described and the project QAPP and sampling plan will be attached. All of the data results will be presented and described relative to the project objectives. We will make recommendations on further data collection, if necessary, and the potential causes and sources of increases in TAH if they occur. Data will be discussed relative to water quality standards and potential impact to aquatic biota. Project success will be determined based upon the completeness of data collection and on whether project objectives were accomplished.

Product: The draft report will be submitted to the DEC project manager by the end of the 3rd Quarter. Comments on the draft document as well as spring data results will be incorporated and a final document submitted prior to the end of July 2009, or as requested by the DEC project manager.

A7. Quality Objectives and Criteria for Measurement of Data

The parameters in the Table 1 will be measured at the indicated performance level. All parameters are critical to meeting project objectives. Criteria for Measurements of Data are the performance criteria: accuracy, precision, comparability, representativeness and completeness of the tests. These criteria must be met to ensure that the data are verifiable and that project quality objectives are met.

Table 1. Accuracy, precision, and completeness objectives for measurement parameters.

| Parameter | Method | Resolution/ Limit | Expected Range | Accuracy% | Precision % | Completeness |
|------------------------------------|-----------------------------|----------------------|-------------------|-------------------------|-------------|--------------|
| рН | Meter | 0.01 | 6.5 to 8.5 | 95 to 105 @ 7.0 | 5% | 90% |
| Turbidity (NTU) | Meter | 0.1 | 1 to 6 | 75 to 125 | 20% | 90% |
| Specific Conductance (μS/cm) | Meter | 0.1 | 100 to 200 | 95 to 105 @ 100μS/cm | 5% | 90% |
| DO (mg/L) | Meter | 0.1 | 8 to 16 | 95 to 105 @ 10mg/L | 5% | 90% |
| TAH (mg/L) | EPA 624 | 0.001 | 0.001 to 0.01 | 75 to 125 | 20% | 90% |
| Total Fecal Coliforms (cfu) | SM9222D | 1 | 0 to 300 | N/A | 25% | 90% |
| Juvenile Fish | Baited minnow traps | 1 | 0 to 50 | N/A | N/A | 90% |
| Macroinvertebrate s | Drift Nets | I | 300 | N/A | N/A | 90% |
| Temperature (°C) | НОВО | 0.1 | 0 to 15 | 97 to 103 @ 15°C | 5% | 90% |
| Discharge (cfs) | Sum of Component Flow | 1.0 | 200 to 600 | N/A | 20% | 90% |
| Boat Counts | Observations | 1.0 | 0 to 20 | N/A | 5% | 90% |

Accuracy

Accuracy is a measure of confidence that describes how close a measurement is to its "true" value. Methods to ensure accuracy of field measurements include instrument calibration and maintenance procedures discussed in Section B of this QAPP.

$$Accuracy = \frac{MeasuredValue}{TrueValue} \times 100$$

Precision

Precision is the degree of agreement among repeated measurements of the same characteristic, or parameter, and gives information about the consistency of methods. Precision is expressed in terms of the relative percent difference between two measurements (A and B).

$$Precision = \frac{(A-B)}{((A+B)/2)} \times 100$$

Representativeness

Representativeness is the extent to which measurements actually represent the true condition. Measurements that represent the environmental conditions are related to sample frequency and location relative to spatial and temporal variability of the condition one wishes to describe.

Comparability

Comparability is the degree to which data can be compared directly to similar studies. Standardized sampling and analytical methods and units of reporting with comparable sensitivity will be used to ensure comparability.

Completeness

Completeness is the comparison between the amounts of usable data collected versus the amounts of data called for.

Quality Assurance for Measurement Parameters Accuracy and Precision

The percent accuracy and precision for the acceptance of data is shown for each parameter in Table 1.

Water Chemistry. Accuracy will be determined for those measurements where actual values are known. For pH, conductivity, turbidity, and dissolved oxygen, measurements of commercially purchased standards within the range of expected values will be used. For dissolved oxygen, 100% saturated air will be used as a standard. The accuracy of sonde turbidity measures will be determined using known standards before and after deployment. Precision will be determined through comparisons with grab samples. Measurement accuracy will be determined for each sampling event. Contract laboratories will provide the results of accuracy measures along with chemical analytical reports. Sample analytical precision will be determined by obtaining a

sample replicate at one site on all sampling dates. For aromatic hydrocarbons, duplicate samples will be collected at all sampling sites on all dates which can be used for additional precision measures if necessary. Trip blanks will be carried on all sampling events to test for contamination from external sources.

<u>Temperature</u>. Accuracy for Stowaway temperature loggers has been calculated to be 0.40°C by the manufacturer, which at 15°C is 97% to 103%. Accuracy will be checked at two known temperatures, 0°C and 20°C, prior to deployment and upon retrieval.

<u>Fish</u>. Fish identification and counts will be assumed accurate. ARRI staff are well trained in the identification of juvenile salmon and other common fish species often captured within minnow traps. Similarly, it is assumed that a repeat count of fish collected within a trap will result in the same value.

Macroinvertebrates. There is no known standard that can be used to check the accuracy of the macroinvertebrate drift samples. Measurement duplicates likely will produce different results. At least three replicates will be collected above and within the heavy use area. Differences in the abundance and community composition of macroinvertebrates will be based on statistical tests and data will be presented as means with standard deviations to demonstrate site variability in macroinvertebrate data.

<u>Discharge</u>. Accuracy cannot be checked against a known value. Precision of measures will be calculated from replicate discharge measures conducted twice each season.

<u>Boat Use</u>. The precision of boat use observations will be calculated by having two independent observers count boat use, motor type and size on the same date and compare results.

Representativeness

The site location, sampling frequency, and timing will ensure that the measurement parameters adequately describe and represent actual stream conditions for the sampling period. Single year data should not be interpreted to be representative of conditions over longer temporal scales. Repeated measures over multiple years are necessary to describe the variability among years.

Comparability and Completeness

The use of standard collection and analytical methods will allow for data comparisons with previous or future studies and data from other locations. We expect to collect all of the samples, ensure proper handling, and ensure that they arrive at the laboratory and that analyses are conducted. Our objective is to achieve 90% completeness for all measures. Sample collection will be repeated if problems arise such as equipment malfunction or lost samples. Due to the size of the Little Susitna River the completeness of some measures may be reduced due to high flows.

A8. Special Training Requirements/Certification Listed

Jeffrey C. Davis (Project Manager) has a B.S. degree in Biology from University of Alaska Anchorage and a M.S. degree in Aquatic Ecology from Idaho State University. He has 12 years of experience in stream research. Mr. Davis has experience in all of the assessment techniques outlined in this document. He has experience in macroinvertebrate collection pursuant to the USGS NAWQA program, the EPA Rapid bioassessment program, modification of these

methodologies for Idaho and Alaska. Mr. Davis also has experience in aquatic invertebrate and vertebrate species identification.

Gay Davis (Quality Assurance Officer) has a B.S. degree In Wildlife Biology from the University of Maine. She has 16 years of experience in stream restoration and evaluation.

Chemical analyses will be conducted through AM Test Inc., in Redmond Washington. AM Test Inc., has been accredited by Washington State Department of Ecology for drinking water, waste water and solid matrix chemical analyses.

With the combined experience of these investigators, no additional training will be required to complete this project.

A9. Documentation and Records

Field data including replicates measures for quality assurance will be recorded in Rite-in-the-Rain field books. Upon returning to the laboratory, the field book will be photocopied (daily or weekly). The field data book will be kept and stored by the Project Manager and the Quality Assurance Officer will store the photocopies. ARRI will maintain records indefinitely. The final data report will include as appendices results of QC checks. Any sampling problems will be recorded on the data sheets and included in the field sampling report. Laboratory reporting and requested laboratory turn around times of 6 to 10 days are discussed in section B4. Laboratory reports will be received as paper and electronic files. Copies of the laboratory reports will be included within the final report.

The project reporting requirements are as follows:

- Quarterly Reports: Quarterly progress, financial, and MBE/WBE reports will be submitted for the periods ending September 30, 2008, December 31, 2008 and March 31, 2009.
 Reports are due 15 days after the final date of the quarter and are considered late if received more than 15 days after these dates. A final progress, financial, MBE/WBE reports, and all required deliverables are due July 31, 2009, and are considered late if received after that date. All reports will be submitted in written and electronic formats requested by DEC.
- Monitoring Data Entry. In addition to a written project report, any water quality monitoring data collected by the project will be provided to the DEC in accordance with the guidance and templates provided at: http://www.state.ak.us/dec/water/wqsar/storetdocumentation.htm. The guidance and templates show the layout required for STORET compatible files and detail the valid values for various fields used in STORET (e.g. characteristics, analytic procedures, HUCs, etc). The data will be provided to DEC electronically via email, CD, diskette, or via an FTP website (to be determined). All data collected by Dec 31, 2008 will be furnished to DEC by March 31, 2009, and all data collected by the project will be furnished to DEC by July 31, 2009.

• Project Photographs. At least 3 electronic photograph(s) of the project will be submitted in a format suitable for publishing. Additional project photos are appreciated. These photos will represent all of the following: the problem the project addresses, the project in progress, and the environmental benefit of the project. At least one of these photos must be submitted with the first quarterly report; the remainder will be submitted with the final report or sooner if available. Each photo will be at least 800 x 600 pixels in size and in JPEG format or other format acceptable to the department. Included will be background information on what the photo represents and when and where it was taken. If possible, the information will be in the photo's file name, such as "Fish_Ck_samplesite1_iron_floc_101608". Alternatively, it may be provided with a caption that states the date, location, and describes the subject: for example "MCV-023X.JPG. Taken 10-16-08, Ditch along south side of Alaska Highway that empties into Fish Creek: Note channelization."

• Final Report Evaluating Project Accomplishments and Benefits:

A final report will be produced that evaluates and describes the project accomplishments and their environmental benefit. These environmental benefits will be determined by the description of the spatial and temporal extent of total aromatic hydrocarbon concentrations within the Little Susitna River adjacent to the Public Use Facility. The environmental benefits will be determined by the description of the spatial and temporal extent of turbidity changes relative to activity surrounding sport fisheries in the lower Little Susitna River.

• <u>Deliverables:</u> (at least 1 electronic and 3 hard copies of each)
In addition to submitting the information identified in the reporting requirements, the following products will be delivered to the Department. All written products will be submitted to the department in both hard copy and electronic format.

| QAPP and Sampling Plan | July 31, 2008 |
|------------------------|----------------|
| Draft Final Report | April 15, 2009 |
| Final Report | July 31, 2009 |

B1. Sampling Process Design

The sampling design consists of obtaining water samples for TAH analyses at river locations and times with heavy boat use and at locations and times with little or no boat use. Background water chemistry and water temperature will be obtained at the same time. Sampling is designed to occur before, during and after the coho salmon fishery in 2008 and before and during the Chinook fishery in 2009. Sampling locations are upstream of and within areas heavily used for boat-accessed fishing. Sampling sites will be located above and below the Public Use Facility. The timing and intensity and type of boat use on the Little Susitna River will be obtained through survey data collected by State Park staff at the Public Use fee station and by observations during water sampling. Turbidity within the heavy use areas will be determined using data loggers and grab samples. One data logger will be placed well upstream of most boat use and provide reference measurements. The second logger will be placed within the heavy use area approximately 2 km below the boat launch. Loggers will be placed on the edge of the thalweg on outside stream bends in water depths of at least 0.5 m.

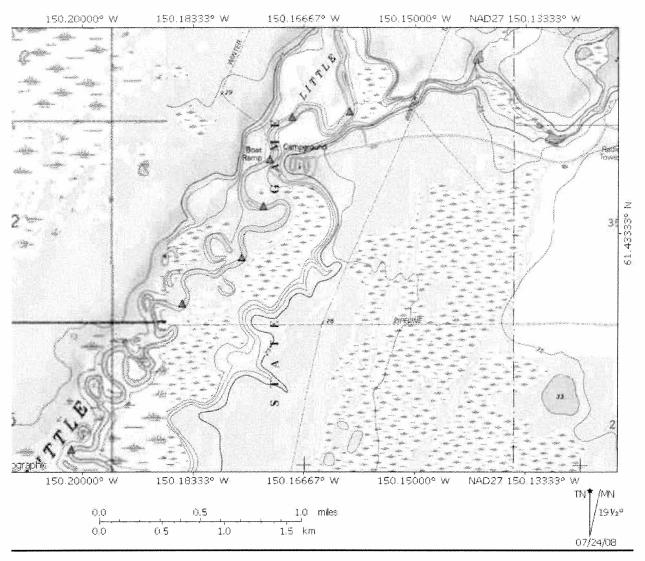


Figure 1. Map of the Little Susitna River in the vicinity of the Public Use Facility and boat launch showing sampling locations (red triangles).

Grab samples will be collected concurrent with TAH sampling (at the furthest upstream and downstream locations). Turbidity will be measured at turbidity logger locations upon deployment, battery checks, and removal. The potential influence of elevated TAH concentrations and turbidity on the biotic community will be determined through measures of macroinvertebrates and fish. Macroinvertebrates will be collected from the drift at reference and heavy use areas. Juvenile salmon will be captured in baited minnow traps from reference and heavy use areas.

Sampling Locations

The sampling locations for TAH will be distributed from 1.0 km above the public use site to 4.0 km downstream. Samples will be collected from 1.0 km and 0.5 km above the boat launch, at the boat launch, and 0.5 km, 1.0 km, 2.0 km and 4.0 km below the boat launch (Figure 1). Basic

water chemistry will be conducted at two locations (furthest upstream and furthest downstream sampling locations).

Continuous measures of turbidity, macroinvertebrate, and fish sampling will be conducted above and below the public use site. Reference samples will collected approximately 5.0 km upstream of the boat launch, which is above most boat-accessed fishing. Samples within the heavy use area will be collected approximately 2.0 km below the public use site.

Discharge will be measured 1.0 km upstream of the boat launch. Observations of boat use by motor type will be conducted at the boat launch.

Sample Parameters

Water samples collected weekly from the seven sampling sites will be analyzed for the following parameters.

- pH. This is a measure of hydrogen ion activity. pH is controlled by the rock weathering, buffering capacity of the water, and influenced by biotic respiration. pH will be measured in the field using a calibrated portable meter (Hanna HI 9023 or equivalent).
- Turbidity (NTU). This measures the reflective properties of the water sample relative to the amount of organic and inorganic particles. Turbidity will be measured in the laboratory from grab samples using a Turbidimeter (LaMotte TC-3000e) and *in situ* using Hach Minisonde MS5.
- Specific Conductance (μS/cm). Specific conductance is the inverse of electrical resistance and is relative to the concentration of ions in water. Specific conductance is used as a surrogate for Total Dissolved Solids. Specific conductance will be measured in the laboratory using a conductivity probe and meter (Sper Scientific 840039 or equivalent).
- Dissolved Oxygen (mg/L). Oxygen concentration and percent saturation will be measured using membrane electrode (YSI 550A) in the field.
- Total Aromatic Hydrocarbons (Gasoline)—Water samples will be collected by ARRI and submitted to AM Test Inc. for analyses using EPA 624 methodology. Samples will be collected using the sampler and methodology developed through the U.S. Geological Survey NAWQA program (Shelton 1997). See Appendix A. Duplicate samples will be collected from each sampling site on each sampling date. Field blanks will be collected and trip blanks will be carried and submitted with samples for analyses.
- Temperature (°C). Water temperature will be measured at 15 minute intervals using Water Temp Pro 2 data loggers (Onset Corporation). Temperature loggers will be placed at Millers Reach, and downstream of the public use site.
- Boat use. Boat use at the Public Use Facility is monitored by Alaska State Park staff at the launch fee area. They record the number of boats by date and the approximate boat length. Park staff also will record the type (2-cycle or 4-cycle) of motor. During the hydrocarbon sampling period, we will keep a log of all boats observed, note motor type based on upon cowling wording and size, and duration of time in the reach. If we are unsure of boat motor type, we will attempt to ask the boat owner or place a question mark by the notation.

- Macroinvertebrates. Macroinvertebrates will be collected using drift nets. Three
 replicate drift samples will be collected from reference and potentially impacted
 locations. Samples will be preserved and returned to the laboratory for identification.
 Measures of invertebrate abundance and community composition will be compared
 between locations.
- Juvenile Salmon. Juvenile salmon and other fish will be captured in baited minnow traps. A minimum of 10 baited minnow traps will be fished for 12 to 24 hours. All of the fish will be identified, observed for abnormalities, and measured for fork length.

Sampling Frequency

<u>Water Chemistry.</u> Sampling frequency is designed to provide data before and after heavy use periods. Heavy use occurs during the Chinook and coho salmon fisheries. The Chinook fishery begins the first or second week in June in the lower river near the Public Use Facility and extends into the first week of July. The coho salmon fishery begins near the end of July and extends through August. Sampling will occur weekly for 7 weeks before, during and following the coho fishery and before and during the Chinook fishery.

Table 2. Sampling frequency, location, and timing for each measurement parameter.

| Parameter | Locations | Frequency/samples | Timing | Total Samples * |
|---|-----------|---|---------------------|--------------------|
| ТАН | 8* | Weekly for 7 Weeks in August and September 2008, with biweekly (twice per week) sampling during peak use. Weekly for 7 Weeks in May and June 2009, with biweekly samples during peak use/16 | Mid-Day | 128 |
| pH, Specific Conductance, Turbidity, Dissolved Oxygen | 2 | Concurrent with TAH Sampling/16 | Mid-Day | 32 |
| Water Temperature | 2 | Continuous | 15 minute intervals | N/A |
| Discharge | 1 | Concurrent with water sampling | Mid-Day | 14 |
| Macroinvertebrates | 2 | During peak coho and Chinook fisheries | Mid-Day | 4 |
| Fish | 2 | During peak coho and Chinook fisheries | 12 to 24 hours | 4 |

^{*} includes replicate samples for precision calculations.

Turbidity

The Sonde will be placed within the stream channel to record turbidity at reference and potentially impacted locations for 3 weeks during the fall coho fishery and for 3 weeks during the spring Chinook fishery. The Sonde will be programmed to record turbidity at hourly intervals.

Macroinvertebrates and Fish

Macroinvertebrates and juvenile salmon will be sampled on one day during the peak of the coho fishery and during the peak of the Chinook fishery.

Sample Timing

Water samples will be collected weekly on Saturday or Sunday between 12:00 and 16:00 hours.

External Data

Discharge data will be obtained from the USGS web site (http://nwis.waterdata.usgs.gov/ak/nwis/dv/?site_no=15290000&agency_cd=USGS) and weather data will be downloaded from the National Climate Data Center (http://www.ncdc.noaa.gov/oa/ncdc.html).

B2. Sampling Methods Requirements

Field Data Collection

Field data collection will be conducted by ARRI staff. The latitude and longitude of sampling locations will be recorded and photographs taken upstream, downstream and across the channel at each site. Photographs also will be used to document boating activity and concentration. Sampling will occur on Saturday or Sunday of each week. Measures of dissolved oxygen and pH will be conducted in the field. Samples for turbidity and specific conductance will be collected in clean sample bottles and returned to the ARRI Laboratory for analyses. Samples will be collected from a well-mixed area at each sampling site. TAH sampling will be conducted using the sampler and methods described below, and samples preserved and shipped for laboratory analyses.

pH, Specific Conductance, Turbidity, and Dissolved Oxygen

Depth integrated water samples will be collected in 500 ml sample bottles. The sample bottles will be filled and emptied 3 times before a sample is retained. Water characteristics from well mixed samples will be measured using appropriate meters. Meters, pH, Hanna HI 9023, conductivity, SPER Scientific model 840039, and turbidity, LaMotte TC-3000e. Support equipment will include extra batteries and sample bottles. Clean sample bottles will be used. All meters will be tested and calibrated prior to use. Dissolved oxygen and pH will be measured in situ. Water samples will be returned to the ARRI laboratory for turbidity and specific conductance measures.

Continuous (hourly) measures of turbidity will be collected using a Hach mini-sonde MS5. The sonde will be suspended in the water column from a cable attached to overhanging vegetation.

The sonde will be positioned near the thalweg on the outside of a meander bend. The sonde will be calibrated using turbidity standards prior to deployment.

<u>Materials Required</u>: Data book, pencils, sharpie, 500-ml sample bottles (16 minimum), 60-ml syringe, cooler, gel-paks, pH meter with standards, Hach Sondes, turbidity calibration standard, cable, extra batteries, turbidimeter, dissolved oxygen meter, thermometer, extra batteries, and camera.

Macroinvertebrates

Macroinvertebrates will be captured as they drift within the water column. Drift nets (363 μ m mesh) (3) will be secured below the water surface. A velocity meter (General Oceanics) will be placed within the opening of the net. The drift net will remain in place until velocity at the inlet decreases indicating that the net mesh is filling with debris. The total sample will be transferred to a sample container (500 ml nalgene bottle) labeled (site name, location, date, replicate) and preserved with ethanol. The sample will be returned to the laboratory. All invertebrates will be removed from the sample and identified to the lowest taxonomic level, generally genus.

Materials Required: Drift nets, rebar or metal fence posts, flagging, bucket, 250 μm sieve, sample bottles, labels, ethanol, and hammer.

Juvenile Salmon

Fish will be collected in 10 baited minnow traps soaked for 12 to 24 hours. Captured fish will be identified, measured to fork length, and observed for deformities, eroded fins, lesions or tumors (DELT anomalies) using the USGS NAWQA methodology (Moulton II et al. 2002).

<u>Materials Required</u>: Minnow traps, salmon roe, buckets (2), small net, plastic bags, collection permit, measuring device.

Total Aromatic Hydrocarbons (TAH)

Samples will be collected in accordance with the USGS report "Field guide for collecting samples for analysis of volatile organic compounds in stream water for the national Water Quality Assessment Program (USGS Open File Report 97-401)." This report contains detailed instructions on sample collection procedures (Appendix A) using the USGS-designed VOC sampler distributed by Wildco. Prior to sample collection, the VOC sampler will be decontaminated in Alconox (or similar detergent) and rinsed thoroughly in the river for a few minutes.

Samples will be collected in sample bottles obtained from the contract laboratory. One sample to be analyzed for TAH will be collected (2 vials) from each lowering of the sampler. Samples will be collected at least 12 cm below the water surface and away from any observable sheen. Sampling locations will be accessed by boat or foot. When sampling from the boat, the boat will be anchored, the motor turned off for 5 minutes prior to a sample being collected upstream off of the bow. The samples will be collected adjacent to the thalweg. A rope will be attached to the sampler cables and the sampler lowered into the flowing water until the sampler opening is at 0.5 stream depth. The attached rope and weighted sampler will be used to keep the sampler upright.

HCl acid, provided by the contract laboratory, will be added to each vial after sample collection for preservation and capped (~l drop). Clean vinyl gloves will be worn at all times when handling sampling bottles. The samples will be checked to ensure that there are no air bubbles after capping. The sample bottles will be dried, labeled using adhesive labels, placed within a cooler on frozen gel-paks and shipped to the contract laboratory. Sample temperatures will be recorded by the contract laboratory upon receipt using a laser thermometer. Trip blanks provided by the contract laboratory will accompany the sample bottles during collection, shipping, and analyses. Field blanks will be collected at the end of each sampling event by submerging the sampler in a stainless steel pot filled with municipal well water.

<u>Materials Required</u>: Sample bottles, labels, hydrochloric acid, dropper, Alconox, VOC sampler, rope and carabineer, gel-paks, cooler, thermometer, 100 ml water bottle, laboratory chain-of-custody forms, and gloves.

Temperature

Stream water temperature data loggers will be placed within the stream at two locations. Loggers will be secured to the bank using plastic coated wire rope. Loggers will be downloaded at least monthly.

<u>Materials Required</u>: 4-m sections of wire rope, clamps, temperature data loggers with backup, software, base station, coupler, and shuttle.

Discharge

Discharge will be measured using the sum of individual components method of Rantz et al. (1982). Velocity will be measured using a Swoffer 3000 velocity meter and wading rod. Lateral distance will be measured using a meter tape or distance finder.

Materials Required: Velocity meter and wading rod, and distance finder or 50-meter tape.

B3. Sample Handling and Custody Requirements

Water samples will be labeled in the field. Sample labels will record the date, time, location, preservation, and initials of collector. Chain of custody forms will be initiated in the field and completed each time samples are transferred to a laboratory, or other carrier. Field samples that are to be transferred to the contract laboratories will be placed within a cooler and the cooler sealed closed using plastic packing tape. Samples will be transported or shipped to the laboratory where they will be placed in a secure location until analyses are completed.

B4. Analytical Methods Requirements

Sample analytical methods are shown in Table 3. Field samples will be collected by ARRI staff and delivered to the commercial laboratory for subsequent analyses by the identified standard method. Dissolved oxygen and pH will be measured in the field. Turbidity and specific conductance will be analyzed at the ARRI laboratory.

Corrective Action

ARRI will be responsible for ensuring that all samples are collected and delivered to the laboratory. The QA officer will make sure all samples are labeled and stored correctly and that all equipment has been calibrated and accuracy tests completed as needed. The Project Manager will be informed of any errors and will be responsible for corrective action including repeating sample collection or analyses (for metered measures). If any samples are lost or are determined to be contaminated by the laboratory or if there are any laboratory problems, the Project Manager will be responsible for collecting new samples and delivering them to the laboratory.

Table 3. List of Analytical methods and detection limits for study parameters.

| Table 3. List of Analytical methods and detection limits for study parameters. | | | | |
|--|---------------|-----------------------|---------------|-------------|
| Measurement | Collection/ | Method | Limits | Turnaround |
| | Analyses | | | Time (days) |
| Total Aromatic | ARRI/ AM Test | EPA 624 | 0.001 mg/L | 14-21 |
| Hydrocarbons | Inc | | | |
| Temperature | ARRI | Temperature | 0.1 Degree C | Weekly |
| | | logger | | Download |
| рН | ARRI/ARRI | Meter (Hanna HI 9023) | 0.01 pH units | 15 minutes |
| Conductivity | ARRI/ARRI | Meter (SPER | 0.1 mhos (0 | 1 |
| | | 840039) | to 200) | |
| | | | 1.0 mhos | |
| | | | (>200) | |
| Turbidity | ARRI/ARRI | Meter (HACH | 0.1 NTU (0 to | 1 |
| | | Model 16800) | 10) | |
| | | | 1.0 NTU (10 | |
| | | | to 100) | |
| Dissolved Oxygen | ARRI/ARRI | Meter (YSI Model | 0.01 mg/L (0 | 15 minutes |
| | | 55) | to 20) | |
| Discharge | ARRI | Swoffer 3000 | 0.1 cfs | 1 |
| - | | Velocity Meter | | |
| Macroinvertebrates | ARRI | Invertebrate Drift | 1 | 6 Months |
| | | (Hauer and Resh | | |
| | | 2007) | | |
| Fish | ARRI | Minnow Trap | 1 | 1 |

B5. Quality Control Requirements

The following table (Table 4) lists the percent of field and laboratory replicates to be used for quality control (See section A7 for discussion on calculation of precision and accuracy). If accuracy and precision are not met for the analyses ARRI is conducting, the meters will be recalibrated and measures will be repeated or meters or probes will be replaced. Data measurements that do not meet the limits described in A7 may or may not be used in the final report depending on degree to which limits are not met. However, the report will clearly state if there are any questions regarding used data.

B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Instruments and meters will be tested for proper operation as outlined in respective operating manuals. Inspections and calibration will occur prior to use at each site. Equipment that does not calibrate or is not operating correctly will not be used. For most parameters (temperature, conductivity, discharge, and pH), duplicate instruments and meters are available. In the case of complete equipment failure, new equipment will be purchased. The VOC sampler is on loan from the State of Alaska. The sampler is of simple and sturdy construction. If damaged we will first, attempt to repair the sampler, second, attempt to borrow a second sampler from the State, and if none are available, we will work with DEC to develop an alternative sampling method The Project Manager will be responsible for calibrating, testing and storing equipment and completing log sheets. All calibrating, testing and storage will follow the manufacturer's recommendations. The QA Officer will inspect the log sheets. Spare batteries and repair equipment will be taken during field sampling events.

Table 4. Field and laboratory replicates for quality control.

| Parameter | Field Replicates | Laboratory Replicates | Comments |
|--|------------------|-----------------------|---|
| pH, Specific Conductivity, Turbidity, Dissolved Oxygen | 14 % | 14% | Replicate measurements one of every 7 samples. |
| ТАН | 14 % | 10% | Duplicate sample collected at one of the sites and a trip blank for every sampling event. |
| Temperature | 1% | None | Water temperature will be measured on each sampling event with meters and compared with temperature logger readings. Loggers will be placed in the same location for 24 hours and reading compared. |
| Discharge | 10% | N/A | Duplicate discharge measure will be collected on every 10 th sampling date (twice each field season). |
| Macroinvertebrates | N/A | N/A | Replicate samples will be collected to determine variability. |
| Fish | N/A | N/A | 10 replicates will be collected to determine variability in catch rate. |

B7. Instrument Calibration and Frequency

The pH meter, conductivity meter, dissolved oxygen, and turbidity meter will be calibrated in accordance to instructions in the manufacturer's operations manual by the Project Manager prior to each use and a log will be maintained documenting calibration. The velocity meter will be calibrated and checked for accuracy following the manufacturer's recommendation. Calibration will be checked monthly. Standards are required for pH, and turbidity and conductivity.

B8. Inspection/Acceptance Requirements for Supplies and Consumables

Sample containers will be obtained from AM Test Inc. Any needed standards for equipment calibration will be purchased directly from the equipment manufacturer if possible or from a well established chemical company. The QA officer will be responsible for ensuring that standards are not outdated and for the purchase of replacements. The date and source of all purchased materials will be recorded within a separate file for each piece of equipment and kept on file by ARRI along with equipment calibration records.

B9. Data Acquisition Requirements for Non-Direct Measurements

Discharge data will be obtained from the USGS web site (http://nwis.waterdata.usgs.gov/ak/nwis/dv/?site_no=15290000&agency_cd=USGS) and weather data will be downloaded from the National Climate Data Center (http://www.ncdc.noaa.gov/oa/ncdc.html) for the Anchorage Airport. Data from both of these sources will be assumed accurate for the locations where collected. Flow data from the USGS site located near Hatcher Pass will be compared with direct measures to determine whether it is representative of sampling locations.

B10. Data Management

Field data will be entered onto rite-in-the-rain books. The Quality Assurance Officer will copy the field books and review the data to ensure that it is complete and check for any errors. Field and laboratory data sheets will be given to the Project Manager. The Project Manager will enter data into Excel spreadsheets. The Quality Assurance Officer will compare approximately 10% of the field and laboratory data sheets with the Excel files. If any errors are found they will be corrected and the Project Manager will check all of the field and laboratory data sheets with the Excel files. The Quality Assurance Officer will then verify correct entry by comparing another 10% of the sheets. This process will be repeated until all errors are eliminated. The Project Manager will then summarize and compare the data. The Quality Assurance officer will review any statistical or other comparisons made. Any errors will be corrected. The Project Manager will write the final report, which will be proofed by the Quality Assurance officer and submitted to the DEC Project Manager.

Along with presenting project data in easy to understand tables and graphs in the final project report, the water quality data will be provided to DEC in a modernized STORET compatible format. Data will be formatted into STORET compatible files as described at the following DEC web site (https://www.dec.state.ak.us/water/wqsar/storetdocumentation.htm).

C1. Assessments and Response Actions

Project assessment will primarily be conducted through the preparation of reports for DEC by the Project Manager. Section A6 contains more information on the type and date of each required report. At that time the Project Manager will review all of the tasks accomplished against the approved workplan to ensure that all tasks are being completed. The Project Manager will

review all data sheets and entered data to make sure that data collection is complete. If necessary, data collection processes or data entry will be modified as necessary. Any modifications of the data collection methods will be reviewed against the processes described within the QAPP to determine whether the document needs to be updated.

The Quality Assurance Officer will check on contractor's laboratory practices to ensure that samples are handled correctly and consistently. The final report will contain an appendix that will detail all of the QA procedures showing precision and accuracy. Representativeness, completeness, and comparability will be discussed in the body of the report. Any QA problems will be outlined and discussed relative to the validity of the conclusions in the report. Any corrective actions will be discussed as well as any actions that were not correctable, if any.

The QA officer will report to ARRI management any consistent problems in data collection, analyses, or entry identified either internally or through a 3rd party audit. ARRI management will be responsible for developing and implementing a course of action to correct these problems. Where consistent problems may have affected project validity, these will be identified and reported to the DEC Project Manager directly and included in project reports as directed.

C2. Reports to Management

Quarterly Reports will be prepared by the ARRI Project Manager and distributed to the Department of Environmental Conservation Project Manager. Reports will update the status of the project relative to the schedule and tasks of the work plan. Reports include Quarterly Reports, Draft Final Report, and Final Report. The Project Manager will prepare the draft and final reports. The final report also will be submitted in electronic format. Any potential problems with data due to QA will be identified and reported in all submitted reports.

D1. Data Review, Validation, and Verification

The Project Manager and the Quality Assurance Officer will conduct data review and validation. This process for data review is described under section B10 and A7. Data that are obtained using equipment that has been stored and calibrated correctly and that meets the accuracy and precision limits will be used. Data that does not meet the accuracy and precision limits may be used; however, we will clearly identify these data and indicate the limitations.

D2. Validation and Verification Methods

The Project Manager and the Quality Assurance Officer will conduct data validation and verification. The Project Manager will enter all data from laboratory and field data sheets into Excel worksheets. The Project Manager will double-check all entries to ensure that they are correct. The Quality Assurance Officer will compare 10% of the laboratory and field data sheets with the Excel worksheets. The Project Manager will enter all formulas for calculation of parameters and basic statistics. All of these formulas will be checked by the Quality Assurance Officer. If any errors are found, the Project Manager will correct the errors and then check all entries. The Quality Assurance Officer will then repeat a check of 10% of the data entry and all of the formulas and statistics. This process will be repeated until any errors are eliminated. The

Project Manager will organize and write the final report. The Quality Assurance Officer will check the results in the report and associated statistical error (i.e. standard deviation and confidence interval) against those calculated with computer programs. Any errors found will be corrected by the Project Manger.

D3. Reconciliation with User Requirements

The project results and associated variability, accuracy, precision, and completeness will be compared with project objectives. If results do not meet criteria established at the beginning of the project, this will be explicitly stated in the final report. Based upon data accuracy some data may be discarded. If so the problems associated with data collection and analysis, or completeness, reasons data were discarded, and potential ways to correct sampling problems will be reported. In some cases accuracy project criteria may be modified. In this case the justification for modification, problems associated with collecting and analyzing data, as well as potential solutions will be reported.

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Appendix A. USGS Open File Report 97- 401

FIELD GUIDE FOR COLLECTING SAMPLES FOR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN STREAM WATER FOR THE NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

By Larry R. Shelton

U.S. GEOLOGICAL SURVEY Open-File Report 97-401

Sacramento, California 1997

U.S. DEPARTMENT OF THE INTERIOR BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY Gorden P. Eaton, Director

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CONTENTS

Glossary

Abstract

Introduction

<u>Overview</u>

Preparation for sample collection

Site selection

Sampling Equipment

Sampler

Support Equipment

Equipment cleaning

Sample collection procedures

Preparation

Routine sampling

Dip sampling

Sample processing procedures

Field measurements

Quality assurance and quality control

Field blanks

Trip blanks

Field-matrix spikes

Replicate samples

Documentation

Sample identification

Shipping

References cited

Appendix - Selected technical memorandums

FIGURES

1. Schematic of the volatile organic compound (VOC) sampler.

TABLES

- 1. List of volatile organic compound analytes for the National Water-Quality Assessment Program
- 2. List of equipment and supplies for collecting and processing stream-water volatile organic compound (VOC) samples

CONVERSION FACTORS, ABBREVIATIONS, AND ACRONYMS

Conversion Factors

| Multiply | Ву | To obtain |
|-----------------------------------|-------------------------|------------------------------|
| foot (ft) gallon (gal) inch (in.) | 0.3048 3.785 25.4 | meter liter millimeter |

Temperature is given in degrees Celsius (C), which can be converted to degrees Fahrenheit (F) by the following equation: F=1.8(C)+32

Abbreviations

L, liter mg/L, microgram per liter mL, milliliter lb, pound

ASR, analytical services request

DIW. deionized water

FS, field spike

FSR, field-spike replicate

HCL, hydrochloric acid

ID, identification

QA, quality assurance QC, quality control VBW, pesticide/volatile blank water VG, VOC grade blank VOC, volatile organic compound

Acronyms

NAWQA, National Water-Quality Assessment NWQL, National Water Quality Laboratory USGS, U.S. Geological Survey WRD, Water Resources Division

GLOSSARY

Environmental Setting -- Land areas characterized by a unique, homogeneous combination of natural and human-related factors, such as row-crop cultivation on glacial-till soils.

Gaging station -- A fixed site on a stream or river where hydrologic and environmental data are collected.

Indicator Sites -- Stream sampling sites located at outlets of drainage basins with relatively homogeneous land use and physiographic conditions. Basins are as large and representative as possible, but still encompassing primarily one Environmental Setting (typically 50 to 500\x11km2).

Integrator Site -- Stream sampling sites located downstream from drainage basins that are large and complex and commonly contain multiple Environmental Settings. Most Integrator Sites are on major streams with drainage basins that include a substantial portion of the Study Unit area (typically, 10 to 100 percent).

Point sample -- A sample collected at a single point in the stream cross section and at a single point in the stream vertical.

Study Unit -- A major hydrologic system of the United States in which NAWQA studies are focused. NAWQA Study Units are geographically defined by a combination of ground- and surface-water features and usually encompass more than 10,000 km2 of land area. The NAWQA design is based on assessment of these Study Units, which collectively cover a large part of the Nation, encompass the majority of population and water use, and include diverse hydrologic systems that differ widely in natural and human factors that affect water quality.

Water-Column Studies -- Assessment of physical and chemical characteristics of stream water, including suspended sediment, dissolved solids, major ions and metals, nutrients, organic carbon, and dissolved pesticides, in relation to hydrologic conditions, sources, and transport.

Field Guide For Collecting Samples For Analysis of Volatile Organic Compounds In Stream Water For The National Water-quality Assessment Program

By Larry R. Shelton

Abstract

For many years, stream samples for analysis of volatile organic compounds have been collected without specific guidelines or a sampler designed to avoid analyte loss. In 1996, the U.S. Geological Survey's National Water-Quality Assessment Program began aggressively monitoring urban stream-water for volatile organic compounds. To assure representative samples and consistency in collection procedures, a specific sampler was designed to collect samples for analysis of volatile organic compounds in stream water. This sampler, and the collection procedures, were tested in the laboratory and in the field for compound loss, contamination, sample reproducibility, and functional capabilities. This report describes that sampler and its use, and outlines field procedures specifically designed to provide contaminant-free, reproducible volatile organic compound data from stream-water samples.

These guidelines and the equipment described represent a significant change in U.S. Geological Survey instructions for collecting and processing stream-water samples for analysis of volatile organic compounds. They are intended to produce data that are both defensible and interpretable, particularly for concentrations below the microgram-per-liter level. The guidelines also contain detailed recommendations for quality-control samples.

INTRODUCTION

One of the goals of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) (Hirsch and others, 1988) is to establish a network of comprehensive and integrated urban water-quality studies to develop an understanding of the occurrence, significance, sources, movement, and fate of environmental chemicals in urbanized hydrologic systems (Lopes and Price, 1997; Squillace and Price, 1996). The occurrence of many contaminants, including volatile compounds, are being assessed in urban areas. For the information to be comparable among studies in different parts of the Nation, consistent procedures and equipment specifically designed to produce contaminant-free, reproducible volatile organic compound (VOC) data from stream-water samples are critical.

The assessment of VOCs in stream water is part of the Water-Column Studies (Gilliom and others, 1995), which focus on assessing the occurrence, concentrations and seasonal distribution of VOCs (Lopes and Price, 1997). The purpose of this report is to describe the equipment used to sample VOCs in streams and the procedures for using the VOC sampler. Companion reports by Koterba and others (1996) outline the procedures used for collecting VOC samples in groundwater, and Majewski and Capel (1995) discuss sampling of pesticides in the atmosphere.

The glossary at the front of this report includes brief definitions of some terms used in this report. Key terms used to describe the NAWQA Program are capitalized. Trade names used in connection with equipment or supplies do not constitute an endorsement of the product.

OVERVIEW

The sampling designs for stream-water studies rely on coordinated sampling of varying intensity and scope at two general types of sites, Integrator Sites and Indicator Sites. Integrator Sites are chosen to represent water-quality conditions of streams and rivers in the large basins affected by complex combinations of land-use settings, point sources, and natural influences. Indicator Sites, in contrast, are chosen to represent water-quality conditions of streams with relatively homogeneous land use and, usually, are associated with smaller basins in specific Environmental Settings. Most, but not all VOC samples will be collected at urban Indicator Sites located in residential and commercial areas. Site selection and sampling strategies for urban Indicator Sites are described in Lopes and Price (1997).

Two primary sampling strategies are used at the selected Integrator and Indicator Sites: (1) fixed interval sampling (usually monthly) characterizes the spatial and temporal distribution of contaminants in relation to hydrologic conditions and contaminant sources, and (2) intensive sampling characterizes seasonal and short-term temporal variability of contaminant transport during high flows and at more frequent fixed intervals.

Most VOCs are man-made compounds that are components of gasoline, by-products of chlorinating drinking water, or solvents. Laboratory analysis is done by the purge-and-trap technique to separate the VOCs from the water matrix, and the quantitation is done by capillary-column gas chromatography/mass spectrometry. Results are reported in micrograms per liter. The USGS National Water Quality Laboratory (NWQL) VOC analysis schedule 2020 will be used. The analytes are summarized in table 1.

PREPARATION FOR SAMPLE COLLECTION

Site Selection

All VOC sampling sites should be at or near streamflow gaging stations because stream discharges associated with contaminant concentrations are needed to evaluate relations between streamflow and water-quality characteristics (Gilliom and others, 1995; Lopes and Price, 1997). The sample collection site should not be more than a few hundred feet from the station.

Collection sites should be located in relatively straight channel reaches where the flow is uniform. Collecting samples directly in a ripple, or from ponded or sluggish water, should be avoided. Sites directly upstream or downstream of confluences or direct sources of contamination also should be avoided to minimize problems caused by backwater effects or poorly mixed flows. In addition, samples collected downstream from a bridge can be contaminated by runoff from the road surface. Proper field judgement is crucial to achieve a sample representative of the typical environmental conditions.

Samples should be collected at the centroid of the stream in the same cross section throughout the project. This will eliminate many of the potential problems that might arise during the interpretation of the data. This does not mean that the same section used during the low-water wading stage must be used during higher stages that require the use of a bridge or cableway.

However, the flow characteristics at different cross sections can result in incomparable data if the cross sections are not located near each other or in the same flow regime. Rapidly changing stage, discharge, and constituent concentrations dictate that sampling schemes and techniques be planned carefully in advance to ensure that representative samples are obtained.

Table 1. List of volatile organic compound analytes for the National Water-Quality Assessment Program.

[CAS, Chemical Abstract Service number; PCODE, USGS Parameter Code]

| | boratory ana | alyses: Schedule Number 2020 |
|---------------------|----------------|--|
| | PCODE | |
| Halogenated | Alkanes | |
| 630-20-6 | 77562 | 1,1,1,2-Tetrachloroethane |
| 71-55-6 | | 1,1,1-Trichloroethane |
| 79-34-5 | 34516 | 1,1,2,2-Tetrachloroethane |
| 76-13-1 | 77652 | 1,1,2-Trichloro-1,2,2-trifluoroethane |
| 79-00-5 | 34511 | 1,1,2-Trichloroethane |
| 75-34-3 | 34496 | 1,1-Dichloroethane |
| 96-18-4 | 77443 | 1,2,3-Trichloropropane |
| 96-12-8 | 82625 | <pre>1,2-Dibromo-3-chloropropane 1,2-Dibromoethane</pre> |
| 106-93-4 | 77651 32103 | 1,2-Dichloroethane |
| 107-06-2 78-87-5 | 34541 | 1,2-Dichloropropane |
| 142-28-9 | 77173 | 1,3-Dichloropropane |
| 594-20-7 | | 2,2-Dichloropropane |
| 74-97-5 | 77170 77297 | Bromochloromethane |
| 75-27-4 | 32101 | Bromodichloromethane |
| 74-83-9 | 34413 | Bromomethane |
| 124-48-1 | 32105 | Chlorodibromomethane |
| 75-00-3 | 34311 | Chloroethane |
| 74-87-3 | 34418 | Chloromethane |
| 74-87-3 | 30217 | Dibromomethane |
| 75-71-8 | 34668 | Dichlorodifluoromethane |
| 75-09-2 | 34423 | Dichloromethane |
| 67-72-1 | 34396 | Hexachloroethane |
| 74-88-4 | 77424 | Iodomethane |
| 56-23-5 | 32102 | Tetrachloromethane |
| 75-25-2 | | Tribromomethane |
| 75-69-4 | 34488 | Trichlorofluoromethane |
| | 32106 | Trichloromethane |
| Halogenated | | |
| naroyenaced | TITICHED | |
| 75-35-4 | 34501 | 1,1-Dichloroethene |
| 563-58-6 | 77168 | 1,1-Dichloropropene |
| 107-05-1 | 78109 | 3-Chloro-1-propene |
| 593-60-2 | 50002 | Bromoethene |

| 75-01-4 87-68-3 127-18-4 79-01-6 156-59-2 10061-01-5 156-60-5 10061-02-6 110-57-6 | 39175 39702 34475 39180 77093 34704 34546 34699 73547 | Chloroethene Hexachlorobutadiene Tetrachloroethene Trichloroethene cis-1,2-Dichloroethene cis-1,3-Dichloropropene trans-1,2-Dichloroethene trans-1,4-Dichloro-2-butene |
|---|---|--|
| Aromatic Hy | arocarbons | |
| 71-43-2 | 34030 | Benzene |
| 91-20-3 | 34696 | Naphthalene |
| 100-42-5 | 77128 | Styrene |
| Alkyl Benze | nes | |
| 488-23-3 | 49999 | 1,2,3,4-Tetramethylbenzene |
| 527-53-7 | 50000 | 1,2,3,5-Tetramethylbenzene |
| 526-73-8 | 77221 | 1,2,3-Trimethylbenzene |
| 95-63-6 | 77222 | 1,2,4-Trimethylbenzene |
| 95-47-6 | 77135 | 1,2-Dimethylbenzene |
| 108-67-8 | 77226 | 1,3,5-Trimethylbenzene |
| 108-38-3 | 85795 | 1,3-Dimethylbenzene |
| 106-42-3 | | 1,4-Dimethylbenzene |
| 611-14-3 | 77220 | 2-Ethyltoluene |
| 100-41-4 | 34371 | Ethylbenzene |
| 98-82-8 | 77223 | Isopropylbenzene |
| 108-88-3 | 34010 | Methylbenzene |
| 104-51-8 | 77342 | n-Butylbenzene |
| 103-65-1 | 77224 | n-Propylbenzene |
| 99-87-6 | 77356 | p-Isopropyltoluene |
| 135-98-8 | 77350 | sec-Butylbenzene |
| 98-06-6 | 77353 | tert-Butylbenzene |
| Halogenated | Aromatics | |
| 87-61-6 | 77613 | 1,2,3-Trichlorobenzene |
| 120-82-1 | 34551 | 1,2,4-Trichlorobenzene |
| 95-50-1 | 34536 | 1,2-Dichlorobenzene |
| 541-73-1 | 34566 | 1,3-Dichlorobenzene |
| 106-46-7 | 34571 | 1,4-Dichlorobenzene |
| 95-49-8 | 77275 | 2-Chlorotoluene |
| 106-43-4 | 77277 | 4-Chlorotoluene |
| 108-86-1 | 81555 | Bromobenzene |
| 108-90-7 | 34301 | Chlorobenzene |
| Ethers and | other Oxygen | ated Compounds |
| 78-93-3 | 81595 | 2-Butanone |
| 591-78-6 | 77103 | 2-Hexanone |
| 108-10-1 | 78133 | 4-Methyl-2-pentanone |
| 67-64-1 | 81552 | Acetone |

Water Quality Evaluation of the Lower Little Susitna River July 2008
Revision 2.0

| 60-29-7 108-20-3 637-92-3 1634-04-4 109-99-9 994-05-8 | 81576 81577 50004 78032 81607 50005 | Diethyl ether Diisopropyl ether Ethyl tert-butyl ether Methyl tert-butyl ether Tetrahydrofuran tert-Amyl methyl ether |
|--|---|--|
| Others | | |
| 107-02-8 107-13-1 75-15-0 97-63-2 96-33-3 126-98-7 80-62-6 | 34210 34215 77041 73570 49991 81593 81597 | 2-Propenal 2-Propenenitrile Carbon disulfide Ethyl methacrylate Methyl acrylate Methyl acrylonitrile Methyl methacrylate |

Sampling Equipment

Sampler

Obtaining representative VOC samples in flowing streams is a difficult task. Of critical importance is the design and operation of the equipment and the sampling procedure (Brown and others, 1970). Samplers must be designed to collect an unbiased sample of environmental conditions. One important process is to flush atmospheric gases from the sampler before collecting a stream sample (Kilpatrick and others, 1989).

A newly developed VOC sampler designed by the USGS and built by Wildco (fig. 1) will be used to collect stream-water samples for VOC analysis. This sampler has been tested for analyte loss, reproducibility, and carryover contamination in the laboratory and in field settings. The sampler, which is made of noncontaminating materials (stainless steel and refrigeration-grade copper) that will not sorb the analytes of interest, can collect a sample representative of environment conditions in most streams. An important function of the sampler design is to evacuate air and other gases from the sampler before collecting a sample. The VOC sampler weighs 11 lb and can be suspended, by hand, from a short rope or chain while wading a stream. However, when sampling during periods of high flow, 10-lb weights can be added to keep the sampler vertical when it is suspended from a bridge or cableway.

The sampler is designed to collect a sample at a single point in the stream. The stainless-steel sampler holds four 40-mL vials. Copper tubes extend to the bottom of each vial from the inlet ports on top of the sampler. The vials fill and overflow into the sampler body, displacing the air in the vials and in the sampler through the exhaust tube. The total volume of the sampler is eight times larger then the vials; therefore, the vials are flushed seven times (removing the air) before the final volume is retained in the vial. The small (1/16-in. inside diameter) copper inlet ports results in a slow (3 to 4 minutes) filling time. This important design feature helps to produce a representative sample and allows sufficient time to place the sampler at the desired depth. The sampler begins to fill as soon as it enters the stream; however, the final sample is retained in the

vial during the last 15 to 20 seconds of the filling process. A cover over the inlet ports prevents contamination from surface oil and debris when the sampler is removed from the stream.

Figure 1. Schematic of volatile organic compound (VOC) sampler. The sampler body is made of stainless steel, weighs 11 pounds and is 6 inches high. It has an air exhaust tube extending above the sampler, and four copper inlet tubes that extend into four 40-milliliter sample vials.

Support Equipment

Field vehicles are commonly used for more than one purpose (such as streamflow measurements, gaging station maintenance, construction, stream sampling, and sample processing). Sample contamination is more likely to occur when these multiuse vehicles are used to collect and process water samples. Glues and adhesives used in vehicles, and the cabinet construction, can contaminate samples for VOCs. Therefore, it is important that the processing area be free of contaminants, plastics, dirt, fumes, and oil residue. Samples should be removed from the sampler, processed, and capped streamside to avoid possible contaminants in the vehicles. Each vehicle should have a separate storage area for the VOC sampling equipment and supplies. A complete equipment list is given in table 2.

Table 2. List of equipment and supplies for collecting and processing stream-water volatile organic compound (VOC) samples.

[Sources for some items are listed to maintain quality standards. OCALA, USGS Water-Quality Service Unit at Ocala, Florida; NWQL, National Water Quality Laboratory; VG, VOC grade blank; VBW, pesticide/volatile blank water]

Sampling equipment and supplies

```
Volatile organic compound (VOC) sampler (Wildco 990-J98) Vial, glass, amber septum, 40 milliliter (NWQL and OCALA 333FLD) Rope, nylon, 1/4-inch diameter (OCALA 84FLD)
```

Cleaning and storing equipment and supplies

```
Gloves, vinyl, powderless (OCALA 155HWS)
Detergent, phosphate free, 0.2 percent by volume (OCALA 62FLD)
Methanol, pesticide grade
Deionized water
VOC grade blank water (VG or VBW) (NWQL)
Bottles, wash, plastic, for detergent (OCALA 357FLD)
Bottles, wash, Teflon, for VG water (OCALA 377FLD)
Bottles, wash, Teflon, for methanol (OCALA 377FLD)
Basins, wash, plastic (2)
Brush, scrub, soft metallic
Bag, plastic, sealable, medium (OCALA 23FLD)
Storage container, sealable, 8 inches x 8 inches x 12 inches
Foil, aluminum, heavy duty
Container, waste, solvent, 5 gallons
```

Processing equipment and supplies

```
Cannister, stainless steel, 8 quarts with cover (for field blanks) Flask tongs
Gloves, vinyl, powderless (OCALA 155HWS)
Hydrochloric acid 1:1 acid, in Teflon vials (NWQL)
Kit, matrix spike (NWQL)
pH paper (alkacid test ribbon)
Bottle labels (OCALA 84FLD)
Sleeves, foam (OCALA 358FLD)
Coolers, shipping, 1 gallon
Coolers, shipping, 5 gallon s
Bags, plastic, 5 gallons
Ice
```

Miscellaneous equipment and supplies

```
Boots, hip
Waders, chest
Tools
First aid kit
Highway emergency kit
Forms, field documentation (OCALA)
Forms, analytical request (NWQL)
Tissues, laboratory
Pens, marking, permanent, (OCALA 77FLD)
Field meters, conductance, pH, dissolved oxygen
Supplies for field measurements
```

EQUIPMENT CLEANING

All equipment that will come in contact with the sample should be soaked in a dilute phosphate-free detergent solution; rinsed with tap water, VOC grade blank (VG) water, and methanol; and then air dried prior to each field trip and between sites (Shelton, 1994). Detergents and methanol should be used with care to avoid the possibility of the residue contaminating the sample. A thorough native-water rinse is required at each field site before sampling to remove any remaining cleaning agents and to equilibrate the equipment to the sampling conditions. A list of the supplies needed for equipment cleaning is given in table 2, and detailed procedures for cleaning the VOC sampler are outlined below.

- 1. Open sampler.
- 2. Submerge top and base in a 0.2-percent solution of phosphate-free detergent. Scrub the sampler thoroughly with a nylon brush. Use a small squeeze bottle, filled with the detergent, to flush the copper tubing.
- 3. Rinse the sampler thoroughly with warm tap water or deionized water (DIW) to remove all soap residue.

- 4. Using a Teflon squeeze bottle, rinse with a minimum amount of methanol. Place the used methanol in a waste container for proper disposal (see Water Resources Division [WRD] memorandum 94.07, Appendix).
- 5. Allow to air dry (cover loosely with aluminum foil to avoid airborne contamination). If complete air drying is not possible, rinse three times with VG water.
- 6. Wearing vinyl gloves, reassemble the sampler.
- 7. Wrap areas that will come in contact with the sample with aluminum foil, and place in a sealable plastic bag. Use a large sealed container to protect the sampler in storage and during transport.
- 8. Rinse the sampler (without the vials) with 2 to 3 L of native water prior to sampling.

SAMPLE COLLECTION PROCEDURES

Preparation

The timing of the VOC sampling should be planned to avoid possible contamination by other collection and processing activities (such as procedures and equipment that use methanol). Before beginning any other activity collect and process the VOC samples at the site. The entire sampling and processing procedure (removing it from the storage container, loading the sampler, sampling, and acidifying the sample) should be done at streamside, well away from other processing activities.

Routine Sampling

VOC samples should be collected where the stream velocity represents the average flow, which is typically near mid-channel in the cross section. The following procedure is designed to produce a single-vertical point sample. When collecting samples for VOC analyses, special care must be taken to avoid contamination from any oily film and debris floating on the stream surface. The samples should be collected directly into the prebaked 40-mL amber-glass vials as follows:

- 1. Reclean the sampler, if necessary (see 'Equipment Cleaning' section).
- 2. Transport the sampler to the collection site and rinse three times with native water or submerge it in the stream for several minutes.
- 3. In a protected area, away from any direct source of contamination and wearing vinyl gloves, uncap four 40-mL unlabeled vials and place them in the sampler. Secure and lock the sampler top in position. Store the vial caps in a protected area.
- 4. Lower the sampler into the stream near mid-channel to about one half of the total depth at that vertical. Add weights if the stream velocity is great enough to pull the sampler downstream.

- 5. Collect a sample by holding the sampler in one position until the sampler is full. Air bubbles will rise to the surface while the sampler is being filled, but may be difficult to see. This takes about 3 to 4 minutes. The sample will be retained in the vial during the last 15 to 20 seconds of sampling.
- 6. Remove the sampler when bubbles are no longer present or after about 5 minutes, and return to a protected area at the side of the stream for processing.

Dip Sampling

In very shallow streams where the VOC sampler cannot be submerged, a representative sample usually can be obtained manually by immersing an open vial (dip sample) near the centroid of flow. Wearing vinyl gloves, lower a 40-mL vial to about one half of the stream depth. Point the vial into the stream current, remove the cap, allow the vial to fill, then slowly bring it to the surface. Add hydrochloric acid (HCL), carefully cap the vial, and check for air bubbles that may be trapped in the vial. A dip sample should never be taken when it is possible to use the sampler. Consistent procedures will avoid the possibility of a sampling bias.

SAMPLE PROCESSING PROCEDURES

Biodegradation and chemical reactions, such as oxidation and volatilization, can change many of the compounds present in natural waters before analyses in a laboratory. Therefore, samples must be preserved as soon as possible after collection. The method of preserving VOCs includes the addition of 1:1 HCL and refrigeration to 4°C to arrest microbiological activity and to minimize volatilization. Great care must be exercised in the field to prevent compound loss or sample contamination. Because exhaust fumes and adhesives in field vehicles may be a source of contamination, processing samples streamside can best prevent contamination. Evaluate trip and field blanks to confirm that the processing area is appropriate.

To preserve the samples, add 1:1 HCL to lower the pH to 2 or less, and immediately place the vials on ice. To determine the volume of acid to add, collect a hand dipped test sample in a used 40-mL vial. Add HCL to the test sample to lower the sample pH to less than 2.0. Two drops of HCL should be adequate for most conditions; however, some environmental samples may require additional HCL. At no time should you use more than six drops of HCL. Alkacid test ribbons can be used to estimate the pH.

By following this sequence for sample preservation, the risk of contaminating a sample is reduced. Acid should be stored and transported properly (see WRD memorandum 94.06, Appendix). These procedures are summarized below.

- 1. Wearing vinyl gloves, open the sampler carefully at streamside.
- 2. Using metal tongs, slowly lift each vial from the sampler reservoir. Do this carefully to avoid losing the convex meniscus.
- 3. Add drops (usually two, but no more than six) of 1:1 HCL to lower the pH to less than 2, and cap the vial.

- 4. Agitate the vial and check for air bubbles. Discard if bubbles are present.
- 5. Three vials from the same sampler set are required for one complete sample. Resample completely, if necessary.
- 6. Label the samples, wrap each with a foam sleeve, and place them on ice.
- 7. Clean the sampler and store it properly (see 'Equipment Cleaning' section).

The minimum information required on each vial is the site identification (ID) number, date and time sampled, preservation, and schedule number, as shown on the example below:

09498500 04-24-1997 @ 1200 HCL to

FIELD MEASUREMENTS

Water temperature, specific conductance, pH, dissolved oxygen, and alkalinity could change dramatically within minutes or hours after sample collection. Immediate analysis in the field is required if the results are to be representative of in-stream conditions.

Water temperature and dissolved oxygen should be measured directly from the stream, and several readings are required in the cross section to obtain a stream average. A composite stream sample should be collected for specific conductance, pH, and alkalinity. A single field meter that measures specific conductance, water temperature, pH, and dissolved oxygen directly in the stream may be used. Detailed information on the procedures, equipment, and supplies necessary for the field analyses is presented in reports by Shelton (1994) and Wilde and Radtke (in press).

QUALITY ASSURANCE AND QUALITY CONTROL

The sources of variability and bias introduced by sample collection and processing affect the interpretation of water-quality data. Quality-assurance (QA) plans ensure that the data collected are compatible and of sufficient quality to meet program objectives. These guidelines and the Study Unit design guidelines for NAWQA should be used when preparing QA plans. Specific details for QA plans are described by Shampine and others (1992).

Investigators in each Study Unit must document the quality of their data by collecting quality-control (QC) samples. A series of QC samples (blanks, replicates, and spikes) must be obtained during VOC investigations because the quality of the data collected, and the validity of any interpretation, cannot be evaluated without QC data. Detailed procedures for preparing QC samples for VOCs, and the recommended frequencies, are described in Mueller and others (1997).

Field Blanks

Field blanks are used to determine whether (1) equipment-cleaning protocols adequately remove residual contamination from previous use, (2) sampling and sample-processing procedures result

in contamination, and (3) equipment handling and transport periods of sample collection do not introduce contamination. Field blanks for VOCs are collected immediately before processing a routine environmental sample. Load four 40-mL vials into the sampler. Pour VG water into a clean (see 'Equipment Cleaning' section) stainless-steel cannister, and then collect two 40-mL vials from the cannister for the cannister-blank sample. Submerge the sampler containing four 40-mL vials in the cannister and allow to fill. Remove the vials and process the field and cannister blanks in the same manner as the environmental sample. Process the samples using the NWQL analytical schedule for environmental samples. If analytical results indicate carryover of residues, perform additional field tests to determine the source of the contamination. A more rigorous cleaning procedure might be necessary. Field blanks produce the most valuable QC data to evaluate potential contamination.

Trip Blanks

Trip blanks are used to determine whether external VOCs from bottle handling and analytical processes, independent of the field sample processing scheme, are contaminating the samples. Trip blanks are provided upon request and are prepared and distributed to each Study Unit by the NWQL. These trip blanks bottles should be stored and transported with the other bottles used for collecting the environmental sample, and then submitted for analysis in the same manner. Trip blanks should never be opened in the field. If analytical results indicate that samples have been contaminated, additional blanks should be processed to identify the source. Trip blanks should only be prepared with field blanks.

Field-Matrix Spikes

Field-matrix spikes are designed to (1) assess recoveries from field matrices and (2) assist in evaluating the precision of results for the range of target analytes in different matrices. Biases and interferences can result from sample matrices and from other processes that occur from the time the sample vial is preserved in the field to the time the vial is analyzed in the laboratory. After collecting the environmental sample, immediately collect a second set of four vials for the field-matrix spikes and preserve each using HCL. Add a standard spike solution using a microliter gas-tight syringe. Matrix-spike kits (solution and syringe) with instructions are available from the NWQL. Label two vials `FS' (field spike) and two vials `FSR' (field-spike replicate). Record the lot number and volume of the spike solution on the field notes and on the NWQL analytical services request (ASR) form. Send each set of vials-two FS and two FSR-as separate sample sets, including the environmental sample, to the laboratory for analyses.

Replicate Samples

Sample replicates are designed to provide information needed to (1) estimate the precision of concentration values determined from the combined sample-processing and analytical method and (2) evaluate the consistency of identifying target analytes for VOCs. Each replicate sample is an aliquot of the environmental sample collected in the same sampler, processed at the same time, and stored and shipped in the same way. Compare the analytical results to determine if accurate, consistent data can be reproduced.

DOCUMENTATION

All field activities and site information should be documented on standard surface-water-quality field notes (Shelton, 1994). A complete documentation will aid in future analyses of the collected information.

Field notes should include the following information:

- 1. Station name and number.
- 2. Date and time (1 minute earlier than environmental sample).
- 3. Gage height, discharge, or both; stage conditions.
- 4. Type of sample (single-vertical point sample).
- 5. Sampler (VOC sampler).
- 6. Sampling method (bridge, cableway, wading).
- 7. Depth and width of stream at sampling location.
- 8. Location within the cross section (midstream).
- 9. Depth of sampling (mid depth).
- 10. Field analyses and calibration (temperature, conductance, pH, alkalinity, oxygen).
- 11. Detailed alkalinity titration.
- 12. Type of samples collected (VOC, major ions, quality control, and others).
- 13. Name of sample collector(s).
- 14. Site information: color and odor of the stream, weather conditions, and others.

SAMPLE IDENTIFICATION

Consistent specific identification of samples is essential for national data aggregation. For this reason, a data-coding strategy has been developed for the NAWQA Program. Use the following instructions for coding information onto the water quality field notes and on the NWQL ASR forms. The most critical codes for proper sample identification are the station ID number, sample medium, and sample type. Different sample-time coding is specified to distinguish among multiple samples collected during the same site visit. VOC samples will have a time 1 minute earlier than all other environmental samples to segregate the VOC analytical results from other analyses. For QC samples, the time codes are used to establish a rationale for associating the necessary sample codes with each individual sample. Do not use fictitious station ID numbers for routine QC samples.

VOC Environmental Sample

STATION ID - Same as other environmental sample

DATE - Same as other environmental sample

TIME - One minute earlier than the other environmental samples

SAMPLE MEDIUM - '9' (surface water)

SAMPLE TYPE - '9' (regular)

Parameter 71999 (Sample purpose) - `15' (NAWQA)

Parameter 99111 (QA data with sample) - `10' (blank)

Field Blank

STATION ID - Same as environmental sample

DATE - Same as environmental sample

TIME - Exact time of preparation (different from other blanks)

SAMPLE MEDIUM - 'Q' (QA sample, artificial)

SAMPLE TYPE - '2' (blank)

COMMENTS - 'PREVIOUS SAMPLE AT:' station ID, date/time

Parameter 71999 (Sample purpose) - `15' (NAWQA)

Parameter 99102 (Type of blank sample) - `100' (field)

Parameter 99104 (Blank lot number) - Enter first five digits

Parameter 99101 (Source of blank solution) - `10' (NWQL)

Cannister Blank

STATION ID - Same as environmental sample

DATE - Same as environmental sample

TIME - One minute earlier than field blank (different from other blanks)

SAMPLE MEDIUM - `Q' (QA sample, artificial)

SAMPLE TYPE - 'B' (other)

COMMENTS - 'CANNISTER BLANK'

Parameter 71999 (Sample purpose) - `15' (NAWQA)

Parameter 99102 (Type of blank sample) - `100' (field)

Parameter 99104 (Blank lot number) - Enter first five digits

Parameter 99101 (Source of blank solution) - `10' (NWQL)

Trip Blank

STATION ID - Same as environmental sample

DATE - Same as environmental sample

TIME - Exact time of preparation (end of trip)

SAMPLE MEDIUM - 'Q' (QA sample, artificial)

SAMPLE TYPE - '2' (blank)

Parameter 71999 (Sample purpose) - `15' (NAWQA)

Parameter 99102 (Type of blank sample) - '30' (trip)

Parameter 99101 (Source of blank solution) - '10' (NWQL)

Parameter 99109 (Start date YMMDD) - Date blanks received from NWQL

Parameter 99110 (End date YMMDD) - Date trip blanks shipped to NWQL

Field-Matrix Spike

STATION ID - Same as environmental sample

DATE - Same as environmental sample

TIME - `SPIKE (FS)' 6 minutes later than environmental sample (HH:X6)

'SPIKE REPLICATE (FSR)' 7 minutes later than environmental sample (HH:X7)

SAMPLE MEDIUM - 'R' (QA surface water)

SAMPLE TYPE - `1' (spike)

COMMENTS - `FS or FSR', `SCH 9090 spike lot number_____'

Parameter 71999 (Sample purpose) - `15' (NAWQA)

Parameter 99104 (Spike lot number) - Enter first five digits

Parameter 99105 (Replicate type) - `10' (concurrent)

Parameter 99106 (Spike type) - `10' (field)

Parameter 99107 (Spike source) - `10' (NWQL)

Parameter 99108 (Spike volume) - volume used, in milliliters

Replicate Samples

STATION ID - Same as environmental sample

DATE - Same as environmental sample

TIME - Same as VOC environmental sample

SAMPLE MEDIUM - `9' (surface water)

SAMPLE TYPE - '7' (replicate)

Parameter 99111 (QA data with sample) - '30' (replicate sample)

Parameter 99105 (Replicate type) - `10' (concurrent)

Parameter 71999 (Sample purpose) - `15' (NAWOA)

SHIPPING

Samples should be shipped by overnight express mail to the NWQL the same day of collection. A NWQL ASR form must be included with each sample. Place all glass vials in padded sleeves or pack in some other suitable manner to prevent breakage during shipment. Insulated water coolers (1 or 5 gal in volume) make good shipping containers. Chill with an adequate amount of ice to maintain the sample temperature between 0 and 4°C. The amount of ice needed depends on the length of time in transit from field to laboratory and on the season of the year. Ice should be placed inside a double plastic bag in the shipping container. Protect the NWQL ASR form and return labels from the ice by placing them in a sealable plastic bag and fastened it to the inside of the cooler lid with tape. Detailed guidelines on shipping samples are discussed in NWQL memorandum 95.04 (Appendix).

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APPENDIX-SELECTED TECHNICAL MEMORANDUMS

These Water Resources Division (WRD) and National Water Quality Laboratory (NWQL) memorandums are available in U.S. Geological Survey offices, nationwide:

Water Quality Evaluation of the Lower Little Susitna River July 2008 Revision 2.0

WRD 94.06 SAFETY: Storage, transport, handling, and disposal of hydrochloric acid WRD 94.07 SAFETY: Storage, transport, handling and disposal of methyl alcohol NWQL 95.04 OPERATIONS: Shipping to the National Water Quality Laboratory

Back to:

PNSP Publications
USGS Water Resources of California
NAWQA Program

For questions concerning this document, contact: <u>Larry Shelton</u> <!shelton@usgs.gov> *The URL for this page is <http://ca.water.usgs.gov/pnsp/pest.rep/voc.html">*